


ILLINOIS STATE GEOLOGICAL SURVEY

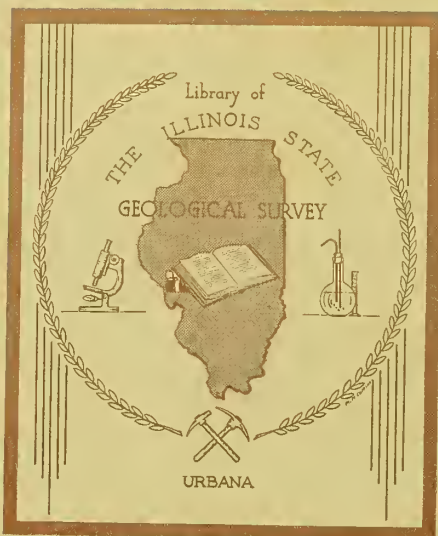


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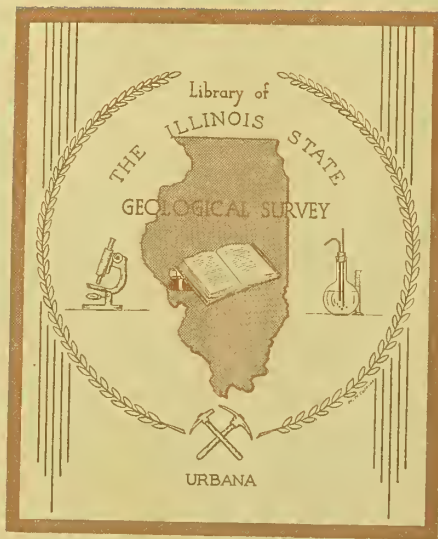
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ILLINOIS STATE GEOLOGICAL SURVEY

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### INTRODUCTION

The radiocarbon dating laboratory of the Illinois State Geological Survey was established in September 1968 to complement the work of the Survey in Pleistocene geology and applied research. As approximately 90 percent of the surface of Illinois is covered by materials whose age is within the range of radiocarbon dating, the service of this laboratory is in great demand. The laboratory routinely processes samples submitted by members of our own staff and by other state agencies. It also processes selected samples from other sources, especially when they are pertinent to Illinois problems.

Even though the radiocarbon dating method has been used by geologists, archeologists, and others in related fields for some time, it is perhaps worthwhile to review the theory and technique and to discuss associated problems common to all radiocarbon dating laboratories, including problems of sampling and contamination. This paper emphasizes in particular the specific procedures and facilities in use at the Illinois State Geological Survey.

### THEORY OF RADIOCARBON DATING

The term "radiocarbon," in general, refers to a naturally occurring radioisotope of carbon,  $^{14}\text{C}$ , which has an atomic weight of 14 atomic mass units and a half-life of 5730 years (Godwin, 1962). Radiocarbon atoms are continuously being produced by the interaction of cosmogenic neutrons and nitrogen in the atmosphere. These atoms are subsequently oxidized to carbon dioxide, which mixes with other carbon dioxide present in the atmosphere. As these processes have been occurring for a very long time, the production of radiocarbon and its decay are in equilibrium, which means that the production rate and the decay



rate are the same. On the basis of these phenomena, Libby undertook research on radiocarbon dating at the University of Chicago that led to his being awarded the Nobel prize in 1960.

Libby made the following assumptions to establish the radiocarbon dating method:

1. Carbon atoms in a dynamic carbon reservoir, which includes the atmosphere, the ocean and other water bodies, and living or decaying organic matter, are in equilibrium.
2. Cosmic ray flux has been constant for a long period of time.
3. No disturbance of the dynamic carbon reservoir has occurred during this long period.

If these assumptions are valid, it should be possible to measure how long ago a carbon sample was separated from the dynamic carbon reservoir system by measuring the difference between the radiocarbon activity of the sample and that of the dynamic carbon reservoir. Libby and his co-workers (Anderson et al., 1947a, 1947b; Anderson, Arnold, and Libby, 1951; Anderson and Libby, 1951; Arnold and Libby, 1949; Grosse and Libby, 1947; Libby, 1955) showed that radiocarbon distribution in the dynamic reservoir is uniform and that the dates of samples of known age essentially agree with the dates determined by radiocarbon measurement, within the experimental error. Thus the radiocarbon dating method was established.

The age of a sample is calculated by means of a formula derived from the radioactivity decay law:

$$t = 18.5 \times 10^3 \log \frac{A_0}{A}$$

where  $t$  = age of the sample in years

$A_0$  = specific activity of the modern standard (95% of NBS oxalic acid specific activity),

and  $A$  = specific activity of a sample.

As the radiocarbon dating method is being used more and more by scientists in their research, its development and refinement have paralleled its usage. More precise measurements with better instruments and more refined chemical processing of samples are making it possible to detect deviations from the previously mentioned assumptions. A brief discussion of these deviations follows.

#### Suess Effect

Suess (1955) observed that the age of late 19th century trees determined from radiocarbon measurements is less than that of trees grown in the early



20th century. He attributed this anomaly to the addition of carbon dioxide to the atmosphere by the combustion of fossil fuels that did not contain radio-carbon because they had been removed from the dynamic carbon reservoir millions of years ago. This effect would make a sample from the first half of the 20th century appear older than its true age.

### Bomb Effect

With the advent of atomic bomb tests, radiocarbon atoms have been artificially produced and introduced into the dynamic carbon reservoir. During the peak period of bomb testing, radiocarbon concentrations 100 percent above normal were commonly reported in the northern hemisphere. This particular effect has produced an opportunity to study the mixing rate of the atmosphere and the equilibria in the dynamic carbon reservoir system. At present the radiocarbon content of the atmosphere is still about 60 percent above normal. Fortunately, determining the "age" of a sample from the post-bomb period does not require the use of radiocarbon dating methods, but a chronological record of radiocarbon content in the carbon system should be kept so that the fluctuations in radiocarbon concentration of environmental material can be correlated with time (Walton and Baxter, 1968). The study of the bomb effect has been carried out by many investigators, including Rafter (1955, 1965), Rafter and Fergusson (1957), Libby (1956), DeVries (1958a), Broecker and Walton (1959), and Broecker and Olson (1961).

### Secular Variation of Radiocarbon Content

A study by DeVries (1958b) revealed some disagreement between ages determined by tree-ring and radiocarbon methods. He observed that radiocarbon activity shows short-term deviations from the expected values, and that these deviations differ according to age and location. Further studies have been carried out by many other scientists (Stuiver, 1961, 1965, 1967; Damon, Long, and Grey, 1966; Suess, 1965, 1967; Dyck, 1965; Kigoshi, 1965; Ferguson, 1968), who have suggested such possible causes of the variations as change of ocean water temperature, sun spot activity, and change of geomagnetism.

Because of the advance made in the field of dendrochronology, radiocarbon ages can be compared with tree-ring ages up to 6,000 B. P. (Before Present), and correction factors are being sought for the periods that show deviations between two ages. The deviation of a radiocarbon age from a known age was expressed as  $\Delta$  or  $\Delta^{14}\text{C}$  by Broecker and Olson (1959, 1961) and as  $d^{14}\text{C}$  by Dorn et al. (1962). Recently, Walton and Baxter (1968) and Kim (in preparation) showed discrepancies in the common usage of these terms, and Kim proposed a new approach for the problem and introduced a new term, D, distinguished from the existing symbols,  $\Delta$ ,  $\Delta^{14}\text{C}$ , and  $d^{14}\text{C}$ .

The calculations commonly used in geochemical studies are expressed as follows:

Broecker and Olson (1959, 1961):

$$\Delta = \delta^{14}\text{C} - (2\delta^{13}\text{C} + 50) \left( 1 + \frac{\delta^{14}\text{C}}{1000} \right)$$

Dorn et al. (1962):

$$d^{14}\text{C} = \delta^{14}\text{C} - 2d^{13}\text{C} \left(1 + \frac{\delta^{14}\text{C}}{1000}\right)$$

Kim (in preparation):

$$D = \delta^{14}\text{C} - 2\Delta^{13}\text{C} \left(1 + \frac{\delta^{14}\text{C}}{1000}\right)$$

where

$$\delta^{14}\text{C} = \frac{A^* - A_0}{A_0} \times 1000$$

$$\delta^{13}\text{C} = \frac{R_s - R_{\text{PDB}}}{R_{\text{PDB}}} \times 1000$$

$$d^{13}\text{C} = \frac{R_s - R_{\text{tree}}}{R_{\text{tree}}} \times 1000$$

$$\Delta^{13}\text{C} = \frac{X_s - X^0}{X^0} \times 1000$$

and where

$A^*$  = the specific activity of a sample corrected for decay due to its age.

$A_0$  = 95% of the specific activity of NBS oxalic acid standard.

$R_s$  = the isotopic ratio of carbon,  $\frac{^{13}\text{C}}{^{12}\text{C}}$ , in a sample.

$R_{\text{PDB}}$  = the isotopic ratio of carbon,  $\frac{^{13}\text{C}}{^{12}\text{C}}$ , in the Chicago PDB standard.

$R_{\text{tree}}$  = the isotopic ratio of carbon,  $\frac{^{13}\text{C}}{^{12}\text{C}}$ , in 19th century standard wood.

$X_s$  = the  $^{13}\text{C}$  abundance of a sample.

$X^0$  = the  $^{13}\text{C}$  abundance of the 19th century wood standard.

Even though several sources of error are inherent in the fundamental radiocarbon dating principle, this method is the most reliable and widely used method in the field of geochronology. The variations would not affect age measurements to the extent that a glacial substage might be misplaced in time sequence.

#### METHODS USED FOR RADIOCARBON DATING

Libby's original solid counting method is no longer used by radiocarbon dating laboratories for routine analysis because more precise methods have been



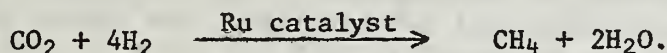
developed. The most widely used radiocarbon measurement techniques are (1) gas counting, in which carbon dioxide, methane, or acetylene is prepared and counted in a proportional counter, and (2) liquid counting, for which benzene is synthesized and counted in a liquid scintillation counter. Both the gas and liquid scintillation procedures start with carbon dioxide from either an organic or inorganic source.

### Gas Counting Method

Sample preparation technique varies somewhat from laboratory to laboratory, but the basic sample processing is the same for all that use the same sample-counting method. The first chemical step is the conversion of the sample to carbon dioxide. Organic samples are burned in a combustion tube in an oxygen atmosphere, and the carbon dioxide is collected and purified. Inorganic carbonate samples are acidified with dilute phosphoric acid to liberate carbon dioxide.

In one method, the pure carbon dioxide from the sample is used directly in a counting instrument to measure the radioactivity of the sample. The detailed procedures of this method were described by DeVries and Barendsen (1952, 1953), Fergusson (1955), Brannon, Taggart, and Williams (1955), and Olsson (1958).

In the methane method (Burke and Meinschein, 1954, 1955; Diethorn, 1956; Fairhall, Schell, and Takashima, 1961), the carbon dioxide is converted according to



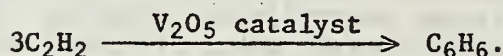
For the acetylene method (Crathorn, 1953; Barker, 1953; and Suess, 1954), the conversion is



### Liquid Counting Method

Radiocarbon dating techniques using liquid sample preparation and liquid scintillation counting were first suggested by Arnold (1954). Acceptance of this method has been somewhat slow due to the elaborate chemical procedure of early methods for preparing liquid samples. Leger et al. (1958), reporting on the synthesis of paraldehyde for liquid scintillation radiocarbon dating, suggested that the ideal liquid sample would be benzene because of its high carbon content and excellent liquid scintillation counting properties. Tamers (1960) and Noakes et al. (1963) developed benzene sample preparation methods suitable for radiocarbon dating. Recent advances in benzene chemistry and liquid counting methods have resulted in a liquid scintillation radiocarbon dating method comparable in performance to gas counting methods. The method used by most laboratories for preparing benzene (Noakes, Kim, and Stipp, 1965; Noakes, Kim, and Akers, 1967) is as follows:





### Comparison of Two Methods

Gas counting and liquid counting methods may be compared only in general terms, as individual laboratories vary in facilities. Gas counting at present tends to be more sensitive than liquid counting because of its lower background conditions (with equal counting efficiencies). This advantage is fast diminishing as highly superior liquid counting devices are now being developed.

Gas counting techniques can accommodate small samples more conveniently, and liquid counting techniques can handle larger samples. If enough sample is available for liquid analysis, as much as 150 ml of benzene can be used. This makes it possible to extend the dating range beyond 60,000 years (Arslanov et al., 1968). Millimole techniques for producing benzene have been developed by Kim, Ikeda, and Ruch (1969), so that smaller samples can be analyzed by liquid scintillation counting techniques.

A comparison of the costs of the two techniques is not possible because of modifications in individual laboratories. The liquid scintillation equipment used by the Survey was purchased in 1968 for about \$15,000. Gas counting apparatus is usually more costly.

### LIQUID COUNTING METHOD USED BY THE ISGS RADIOCARBON DATING LABORATORY

#### Pretreatment of Sample

Samples received by the Survey laboratory are thoroughly inspected, and any obviously foreign material is removed physically. The cleaning process used depends on the type of sample. The object is to remove carbon-containing material that was not part of the sample when the carbon was withdrawn from the dynamic carbon reservoir and incorporated into the material under study—for instance, humic acid in a wood sample, modern rootlets in peat, or inorganic carbonate in organic samples.

Wood samples are first sliced into thin shavings, which are boiled for about 30 minutes with successive amounts of 0.1N sodium hydroxide and 2N hydrochloric acid. The shavings are then washed with distilled water several times and finally dried.

Well preserved charcoal and cellulose-containing peat samples are treated in the same manner as wood samples. Because some carbonized materials,

peat samples, organic silts or clays, and gyttja samples are appreciably soluble in 0.1N sodium hydroxide, they are treated with only a hot solution of 2N hydrochloric acid.

Shell samples are washed in water to remove all foreign material, and a thin layer of surface (~10%) is dissolved with dilute acid to eliminate any surface contamination.

Bone samples are crushed and washed with a hot 0.1N sodium hydroxide solution for 30 to 60 minutes to remove humic acids. Hydrochloric acid (2N) is used to disintegrate the bone and to remove inorganic carbonates. The insoluble fraction (bone collagen) is then collected for combustion.

### Benzene Synthesis

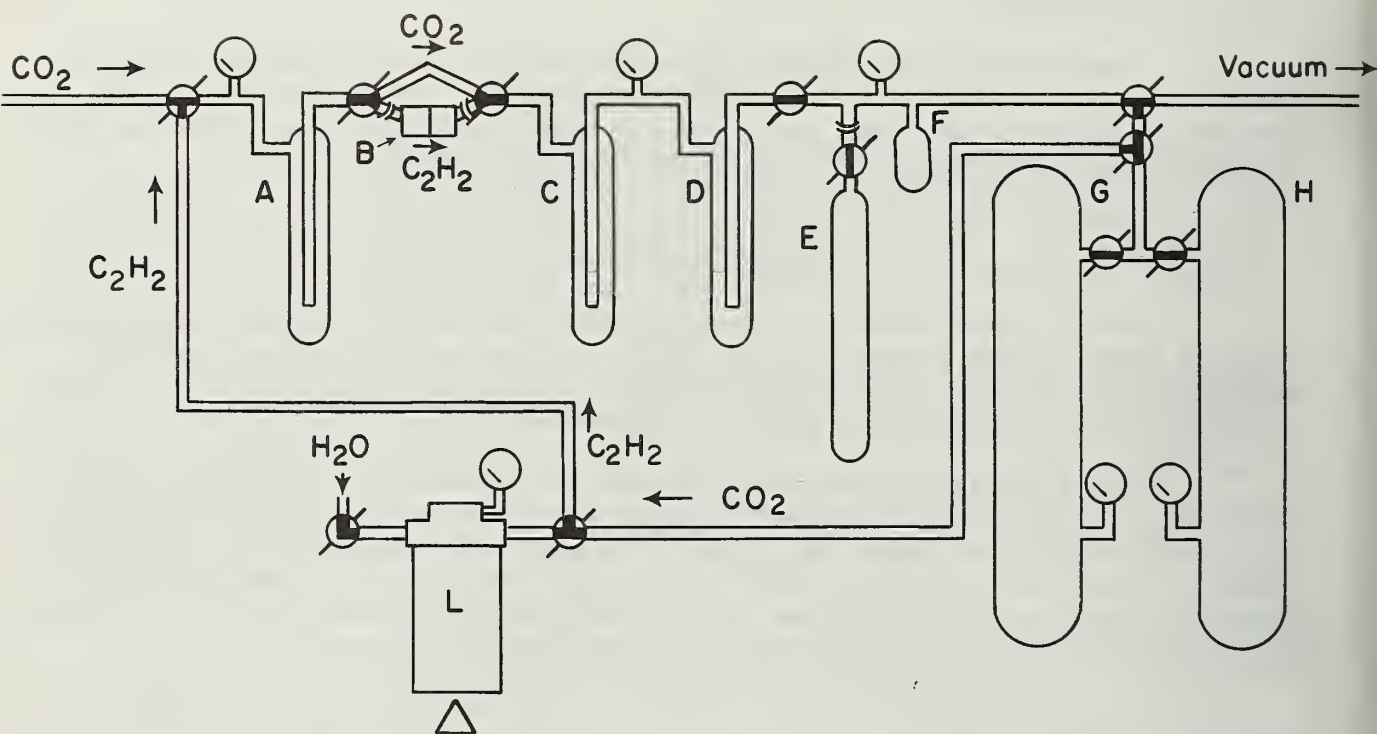
The Illinois Geological Survey laboratory uses the liquid scintillation counting method. The carbon dioxide generated from samples is converted to benzene by the reactions previously described. Each chemical step is discussed in detail below to show how a sample is processed.

The equipment for synthesizing benzene was constructed in the Survey laboratory. Figure 1 is a schematic diagram of the equipment. All columns, traps, connectors, and bulbs are glass. Tubing is polyethylene and the lithium reaction chamber is stainless steel with a glass viewing top. The vacuum and pressure gauge used in the system is an industrial gauge that expresses pressure as pounds per square inch (psi) and vacuum as inches of mercury.

### Sample to Carbon Dioxide

The method used for sample combustion is a modification of Nydal's (1965) method for peat and gyttja. A sample is burned in a stream of oxygen in a combustion tube. Carbon dioxide and carbon monoxide from the combustion are passed over cupric oxide maintained at 600° C and are then absorbed in 6N ammonium hydroxide solution. Upon completion of combustion, 1M strontium chloride solution is added and the mixture is boiled. The strontium carbonate precipitate formed is filtered and washed with 1M strontium chloride solution and distilled water.

Strontium carbonate is acidified with 50 percent (v/v) phosphoric acid to generate carbon dioxide, as are any inorganic carbonate samples that are to be dated. All chemicals used must be free of carbon dioxide. This reaction takes place in a sealed digestion vessel attached to the benzene synthesizer. Carbon dioxide released from the phosphoric acid digestion passes through traps A, C, and D of the benzene synthesizer (fig. 1). Trap A, cooled by Dry Ice and alcohol, removes moisture while traps C and D, cooled by liquid nitrogen, freeze carbon dioxide. In actual operation, carbon dioxide pressure in the digestion vessel is maintained at 400 mm to 700 mm of mercury pressure, shown on the gauge to the left (fig. 1) of trap A. This is accomplished by manipulating the rate of adding acid and adjusting the stopcock to the left of trap C. The stopcock at the right of trap D should be kept closed during the entire carbon dioxide generation step, and the gauge between traps C and D



- |     |   |   |  |
|-----|---|---|--|
| A   | H <sub>2</sub> O freeze trap                                    | L | Lithium reaction chamber               |
| B   | P <sub>2</sub> O <sub>5</sub> and Ascarite<br>purification tube |   | Pressure-vacuum gauge                  |
| C,D | CO <sub>2</sub> and C <sub>2</sub> H <sub>2</sub> freeze traps  |   | Stopcocks                              |
| E   | Catalyst column   |   | Heater                                 |
| F   | Microtrap   |   | Ball-socket ground glass<br>connectors |
| G,H | Gas storage bulbs   |   |  |

Fig. 1 - Schematic diagram of benzene synthesis apparatus used at the Illinois State Geological Survey.



should register a complete vacuum. If any pressure is indicated by this gauge, there is either a leak in the system or evacuation of the system prior to carbon dioxide generation was incomplete.

After carbon dioxide generation is complete, the stopcock for trap D is opened and the trapped solid carbon dioxide is allowed to evaporate into storage bulb G, or into both bulbs G and H, depending on the amount of carbon dioxide present. Residual carbon dioxide in traps C and D is transferred to the storage bulb by freezing it in microtrap F and evaporating it. The amount of carbon dioxide is calculated from the pressure in the storage bulb, the volume of which is known.

#### Conversion of Carbon Dioxide to Acetylene

Carbon dioxide is converted to acetylene by the method described by Barker (1953). Lithium metal shot (2.4 grams per liter (STP) of carbon dioxide, or 1.5 times the stoichiometric amount) is spread over the bottom of the reaction chamber, L (fig. 1), which is evacuated, checked to make sure that there are no leaks, and heated to about 600° C by means of a 1200 watt hotplate. This requires about 30 minutes. Carbon dioxide is then introduced very carefully from storage bulb G. The beginning of the reaction is indicated by the appearance of a red flare over the lithium.

The reaction should be started with the carbon dioxide pressure no higher than 350 mm of mercury in the reaction chamber. However, if the reaction does not begin at 200 mm of mercury carbon dioxide pressure, the temperature of the molten lithium should be raised. The red flare then spreads over the entire body of molten lithium and finally turns to a dull red glow. The carbon dioxide inlet stopcock can then be opened fully and the rate of reaction monitored by the gauge on the reaction chamber. The reaction may take one to two hours for completion.

After the formation of lithium carbide is completed, the heat is turned off and the reaction chamber evacuated for 30 minutes to remove any gases in the system. The chamber is then cooled to room temperature. The lithium carbide is hydrolyzed to form acetylene by introducing distilled water into the cooled chamber. During hydrolysis, hydrogen also is evolved by reaction of water with the excess lithium metal. The acetylene is collected in the same manner as the carbon dioxide in the carbon dioxide process, except that acetylene goes through a phosphorus pentoxide and Ascarite purification tube, B (fig. 1). The hydrogen accumulated in traps C and D must be evacuated by keeping trap C closed and opening the stopcock on trap D. Upon completion of the hydrolysis, acetylene is either evaporated into the storage bulb for trimerization later or is immediately converted to benzene in column E.

#### Trimerization of Acetylene to Benzene

Acetylene is trimerized by using a vanadium-alumina catalyst, as was reported by Noakes et al. (1967). Catalyst pellets are packed in column E, which is 20 cm long and 2.5 cm in diameter. The pellets are activated in a vacuum for 2½ hours at 300° C. Water vapor and other adsorbed gases are

evacuated during this time. The catalyst is cooled to room temperature and the reaction is started by carefully letting the acetylene come into contact with the catalyst.

One method for accomplishing the trimerization is to allow solid acetylene to sublime directly onto the catalyst. *CAUTION! In this method, the pressure must not reach 2 atmospheres because acetylene explodes spontaneously at that pressure.* Usual pressures of operation do not exceed 760 mm of mercury acetylene pressure.

In a second trimerization method, the gaseous acetylene in the storage bulb is allowed to come into contact with the catalyst. The vacuum in the catalyst column will permit acetylene from the storage bulb to flow in and initiate the trimerization reaction. After the reaction has started, a pressure differential between the storage bulb and the catalyst column is maintained because acetylene is trimerized to liquid benzene, thus allowing the acetylene in the bulb to migrate to the catalyst column and sustain the reaction. During the reaction, the temperature of the catalyst column will increase. The rate and the completion of the reaction can be observed from the readings of the pressure gauge between column E and trap F (fig. 1).

On completion of the reaction, catalyst column E is removed, heated to 100° C, and evacuated to extract benzene. A freeze trap (such as A in figure 1) cooled by Dry Ice and isopropyl alcohol is used to collect the benzene. The benzene (usually 1 to 8 ml) is weighed and its radioactivity measured in a liquid scintillation counter. The purity of the synthesized benzene exceeds 99.9 percent.

#### Measurement of Benzene Radioactivity

A modified TRI-CARB liquid scintillation counter, model 3375, from Packard Instrument Company, is used for radioactivity measurements. Additional shielding material around the existing detector shield was added and the external standard radiation source was removed to reduce the external background to a minimum. The background reduction for each step is shown in Table 1.

TABLE 1 - MODIFICATION OF INSTRUMENT AND BACKGROUND REDUCTION

	Background* (cpm)
As received	11.3
External standard removed	10.5
Extra shielding added, 2" of lead	8.8

\* 20 cc sealed glass vial supplied with the instrument.

For routine counting of the sample, the Survey laboratory employs Butyl PBD, 2-(4-tert-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole, as the



scintillator. The counting solution for a 10 ml vial consists of benzene from the sample and 2 ml of toluene containing 100 mg of Butyl PBD. Spectrograde benzene is used for making the total volume to 10 ml when less than 8 ml benzene is produced from a sample.

Each sample is counted for at least a 24-hour period. Sample and background counting are alternated, with the same counting vial used for both counts. A modern standard, 95 percent counting rate of NBS oxalic acid, gives 7.60 cpm/gram of carbon above background activity. Present background activity is  $\sim 6.80$  cpm for a 10 ml vial containing spectrograde benzene.

To prevent possible tritium contamination of the sample from water used during the benzene synthesis, the sample is constantly monitored by measuring the radioactivity of tritium separately.

### PROBLEMS AND ERRORS IN RADIOCARBON DATING

The age determination of a sample is based on a physical measurement and is only as precise as the measuring and sampling techniques used. In a dating laboratory, the specific activity of carbon in the sample is measured and compared with that of standard oxalic acid. An "age" is calculated from the ratio of these specific activities and is reported as, for example,  $5000 \pm 200$  B. P. The standard deviation noted in the above case is  $\pm 200$  years. This means that if the same sample is remeasured, there is 68 percent probability the remeasured age would be in the range of 4800 to 5200 B. P. As was pointed out previously, the "age" is the length of time that the sample has been isolated from the dynamic carbon reservoir with which it was in equilibrium at the time of growth or formation. Any natural changes, such as  $^{14}\text{C}$  fractionation in the equilibrium system, affect the age calculated for a sample. It is possible to correct  $^{14}\text{C}$  isotope fractionation effects in the laboratory by means of a  $^{13}\text{C}/^{12}\text{C}$  ratio factor; however, corrections for the Suess and bomb effects cannot be made.

### Contamination

Possible contamination of the sample after its separation from the system also must be considered. Contamination can be of two types—natural contamination by materials such as modern rootlets and modern carbon added through sample handling. Natural contamination can not be remedied in the field by the collector, but care can usually be taken to eliminate contamination caused by handling. Common causes of contamination by natural phenomena are modern rootlets and humus, allogenic materials in sediment samples, and ground water in carbonate samples. Some types of contaminants can be eliminated by physical or chemical laboratory processes, but others are difficult or impossible to remove. All possibilities that may affect the age determination should be considered and information concerning the sample, the sampling area, and other environmental conditions noted by the sample collector. From this information, a processing laboratory can carry out the necessary steps to eliminate many probable contaminants.



The sources of contamination from sample handling are almost too numerous to mention. Some of the sources are paint chips or grease from tools used for collecting the sample, hair from brushes used for cleaning it, preservatives, polishes, or detergents used on archeological samples, cloth or paper from sample containers, carbon-containing packing material such as cotton or paper, and dust particles.

Samples should undergo a minimum of handling during collection in the field, and extreme care should be exercised to exclude foreign matter from the sample. It is suggested that a sample be placed in a plastic bag, or wrapped in aluminum foil and then placed in a plastic bag. The bag should then be put into a second plastic bag containing a note giving detailed information about the sample, to prevent the paper from coming into contact with the sample. If a sample is moist, it should be dried in a laboratory oven as soon as possible to prevent mold formation, which may cause an error. The dried sample should be stored properly in plastic or foil.

Tables 2 and 3 show the effect of contamination by "infinitely old" carbon, and by modern carbon, respectively. Infinitely old carbon has no detectable  $^{14}\text{C}$  present, whereas modern carbon has the present average specific activity of  $^{14}\text{C}$  in the world's dynamic reservoir. As table 2 shows, if 5 percent of the carbon in a sample is replaced with infinitely old carbon, the apparent age measured would be 400 years older than the true age of the sample. If a sample is contaminated by 1 percent of modern carbon (table 3), samples 600, 5,000, and 60,000 years old would show radiocarbon ages of 540, 4,870, and 36,600 years, respectively.

Considering all the possibilities for contamination, the accuracy of radiocarbon ages may be questioned. However, the scores of interlaboratory check samples that have been analyzed and reported in the journal *Radiocarbon* are generally found to be in good agreement.

#### Standard Deviation

Errors noted in *Radiocarbon* are usually calculated standard deviations and stem from the uncertainty involved in the measurement of radioactivity. Such errors do not include sampling or chemical processing errors associated with the age determination. The error can be decreased by extending counting periods of sample, standard, and background.

Polach and Golson (1966) suggested that the user of reported radiocarbon ages should incorporate in his interpretation two standard deviations instead of the single standard deviation commonly reported. Precision analyses of interlaboratory check samples carried out by Kim (in preparation) showed that the relative error derived from 80 samples analyzed by most of the existing laboratories is  $\pm 5$  percent, suggesting that  $\pm 5$  percent of reported age may be used instead of the reported single standard deviation.

#### Size of Sample

How much sample constitutes an adequate amount for  $^{14}\text{C}$  dating is difficult to specify. Generally, the minimum amount needed is equivalent to 5 grams of

TABLE 2 - EFFECT OF CONTAMINATION BY "INFINITELY OLD"  
CARBON ON TRUE AGE

Contamination (%)	Years older than true age*
5	400
10	830
20	1,800
30	2,650
40	4,100
50	5,570

\* Applies to all true ages.

TABLE 3 - EFFECT OF CONTAMINATION BY MODERN CARBON\* ON TRUE AGE†

True age	Apparent age derived as result of		
	1% contamination	5% contamination	10% contamination
600	540	160	modern
1,000	910	545	160
5,000	4,870	4,230	3,630
10,000	9,730	8,710	7,620
25,000	23,400	19,000	15,500
40,000	32,800	23,200	18,000
60,000	36,600	24,000	18,400

\* Activity of modern carbon is considered the same as 95% of the radioactivity of NBS oxalic acid.

† A detailed graph showing other ages and degrees of contamination was given by Olsson (1968).

carbon. As the amount of sample needed depends on the age of the sample, as much as possible should be collected. Enough should be furnished to permit duplicate analyses to be made. Polach and Golson (1966) and Dyck (1967) pointed out that the amount of sample needed for an analysis would vary according to whether the sample was peat, shell, wood, or other material.

#### APPLICATIONS OF RADIOCARBON DATING METHOD

Radiocarbon dating has been used extensively by investigators in the fields of geology and archeology for some time. In recent years, however, it has been applied to hydrology and environmental pollution. Hanshaw, William, and Rubin (1965) and Tamers (1966) used radiocarbon dating to study ground-water flow velocity and recharge processes. Rosen and Rubin (1965) also used



it to distinguish between industrial and natural pollutants. Recent advances made in liquid scintillation radiocarbon dating have also made it possible to measure tritium concentrations.

If the radiocarbon dating laboratory were considered as a nuclear analytical laboratory specializing in the measurement of low-level concentrations of radiocarbon and tritium instead of merely as a place to make age determinations, its work could be greatly expanded. Radiocarbon methods could be applied to such areas as low-level concentration studies in biomedical sciences, environmental monitoring, and tracing work using both radiocarbon and tritium.

#### RESULTS AND SIGNIFICANCE OF SOME INITIAL ISGS RADIOCARBON ANALYSES

By July 1, 1969, 23 radiocarbon analyses had been completed by the Illinois State Geological Survey Radiocarbon Laboratory. A complete list will appear in *Radiocarbon* with the sample numbers designated by the prefix ISGS.

To establish the accuracy of the new laboratory, splits of three samples dated earlier by other laboratories were obtained and dated (table 4, samples ISGS-3, ISGS-4, ISGS-7), and sample ISGS-12 was submitted to another laboratory after an initial date was obtained at the Illinois State Geological Survey. In addition, a date from an earlier sample (W-406) collected from the same geologic unit and locality as ISGS-12 was also available for comparison. Sample ISGS-17 was collected from the same locality as an earlier dated sample (W-69). In all cases agreement of the Survey dates and those established by the other laboratories was very good, indicating the procedures and equipment used at the Survey could be used with confidence.

One of the first projects of the ISGS dating laboratory was to determine radiocarbon dates for two organic silts from northwestern Illinois that geologic field evidence indicated might restrict the extent of the Woodfordian Green River Lobe (Frye et al., 1969). The two dates, 27,500  $\pm$  500 (ISGS-6) and >27,800 (ISGS-8), from organic silts below surface silts and above the uppermost till that had previously been considered Woodfordian in age, established that the Green River Lobe is less extensive than it had been previously mapped.

Another special project involving radiocarbon dating developed when skeletal remains of a mastodon (*Mammuth Americanum*) were excavated at the edge of Urbana, Illinois. Several bone and ivory fragments were dated, with the following results:

ISGS-17A	Bone, humus fraction not removed	7490 $\pm$ 200
ISGS-17B	Bone, humus fraction removed	8330 $\pm$ 200
ISGS-17C	Ivory, washed with dilute acetic acid, digested with 50% phosphoric acid; carbonate fraction dated	9190 $\pm$ 200

The choice of the benzene-liquid scintillation method for the Survey laboratory was made because it was necessary to establish dates older than



TABLE 4 - INTERLABORATORY CHECK SAMPLES

ISGS Dates		Dates from Other Laboratories	
ISGS-3	38,600 ±200	ORINS-42	39,100 ±600
ISGS-4	30,700 ±400	ORINS-40	28,850 ±400
ISGS-7	11,500 ±300	FSU-3	11,245 ±450
		ANU-5	11,700 ±260
		Tx-541	11,620 ±80
ISGS-12	23,900 ±200	W-406	25,150 ±700
		Tx-693	23,880 ±490
ISGS-17	>40,000	W-69	>34,000

40,000 radiocarbon years. At least two organic zones within the glacial sequence of the state are, at least in part, older than 40,000 radiocarbon years but less than about 60,000 years, as indicated by other evidence. As suitable samples are obtained and refinements made in our equipment and procedures, analyses of these older organic materials should yield dates within the 40,000- to 60,000-year range. Establishment of these dates will aid considerably in resolving several stratigraphic problems within the glacial deposits of Illinois.

Numerous other studies involving radiocarbon analyses are now under way or contemplated for the future. These include the age of pollen sequence in the peat bogs of Illinois and radiocarbon dating of water in hydrogeologic studies.

#### PROCEDURES FOR SUBMITTING SAMPLES TO ISGS RADIOCARBON DATING LABORATORY

A date on an organic sample without additional pertinent information and a specific stated purpose is meaningless. Because no more than about 75 samples per year can be dated with present Survey facilities, rather severe restrictions and a critical screening of samples are necessary. No sample should be submitted "just out of curiosity."

To evaluate and screen the samples, the Survey has established an isotopic analysis committee consisting of three geologists and the radiocarbon analyst. Before a sample can be dated, it must be approved by this committee and by the Chief of the Survey. Certain basic requirements must be fulfilled before a sample is considered. First, a request sheet must be completely filled out and included with the sample. This request must specify the date of sample collection, possible contamination, post-sampling treatment, expected age, references to relevant publications, significance of sample, type of material, description of stratigraphic unit, position and thickness of associated units, and precise location. In addition, the size of the sample and its organic carbon content, its condition, and type of packaging must be such that a radiocarbon determination can be considered.

Having this information, and any additional data the submitter might consider pertinent, the committee reviews the sample and decides whether or not it is of significance. If so, a priority is placed on it with respect to other samples submitted. Strict control over the samples to be analyzed insures that the dates produced will be meaningful.

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